Studies in State-to-State Energy Transfer

Final Report for AFOSR

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Background

The measurement and understanding of the rates at which energy is transferred in intermolecular collisions are problems of long-standing interest in chemical physics. Such processes play a crucial role in many environments: for example, in atmospheric chemistry, especially at high altitudes, in gas lasers, in combustion and in the chemistry of deep space, especially in the characterisation of dense interstellar clouds.

Gas-phase collisional energy transfer is an area in which the Reporter's group has been active for many years. In the past few years, it has been one of several groups world-wide to apply time-resolved double resonance techniques to examine the details of energy transfer at the state-to-state level; e.g. in HCN,[1] C_2H_2[2-4] and NO.[5-7] In Birmingham, these experiments have employed a tunable infrared (IR) laser to promote simple molecules to selected rovibrational states by direct infrared absorption and a tunable ultraviolet (UV) laser to study the subsequent fate of this sub-set of excited molecules as they return to thermodynamic equilibrium with the thermal bath. In general, double resonance methods can be applied to study both *rotational* and *vibrational* energy transfer. Since these two processes usually occur with quite different collisional efficiencies, equilibration over rotational levels within the excited vibrational state is usually complete before significant vibrational relaxation occurs. Consequently, by appropriate choice of the pressure of the sample and the delays between the pulses from the IR pump and UV probe lasers, the rates of both rotational and vibrational relaxation can be measured.

Our first uses of the infrared-ultraviolet double resonance (IRUVDR) technique[1-7] preceded, and was the basis for, the application to AFOSR for support of a novel programme of experiments. At that time it was recognised that a shortcoming of the standard IRUVDR method, and indeed of any other method that has been employed to investigate energy transfer in molecular collisions, is that one can only access rotational levels that have an appreciable thermal population in the vibronic ground state of the molecule. At the heart of our project was the proposal to apply the IRUVDR method to radicals which had just been formed in high rotational levels by a process of photodissociation. It was anticipated that such experiments would provide data that were not only a new and demanding test of theory but that they would also be valuable in understanding the dynamics of processes occurring in the upper atmosphere where both OH[8] and NO[9] are observed in high states of rotational and vibrational excitation.

Our first approach to AFOSR described a rather broad set of experiments in collisional energy transfer. Subsequently, the proposal focused on energy transfer between levels in $OH(X^2\Pi)$. The intention was to generate OH radicals in a broad distribution of rovibrational levels by pulsed laser photolysis of a suitable precursor such as HNO_3 or H_2O_2. Pulses from

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an optical parametric oscillator (OPO) were then to be used to promote OH radicals from high rotational levels in the ($v = 0$) ground vibrational level to high J levels in the ($v = 1$) or ($v = 2$) levels. A frequency-doubled dye laser would be used to observe the kinetic behaviuour of these molecules using laser-induced fluorescence (LIF) on lines in the $A^2\Sigma^+$-$X^2\Pi$ electronic band system of OH.

It was recognised that such experiments were very demanding and, in particular, required improvements in our LiNbO$_3$-based OPO. In the event such improvements have not been forthcoming. This has greatly restricted our ability to perform *three* laser experiments: *i.e.* one for photolysis, one for IR pumping, and one for UV probing. Consequently, although we have performed very successful experiments on relaxation from highly excited levels of NO, determining rate coefficients both for *total* relaxation from levels as high as $J = 40.5$ and for *state-to-state* energy transfer from the same levels of excitation, we have not yet obtained data for OH($X^2\Pi$). For these experients on NO, and those planned on OH, we currently depend on obtaining lasers from the EPSRC Laser Loan Pool located at the Rutherford-Appleton Laboratory.

Despite the fact that we have not yet determined rates of energy transfer in collisions involving OH($X^2\Pi$), we have had several notable successes in our work on energy transfer over the past three years.[10-16] Following a brief description of the experimental methods which have been employed, this work is summarised below under three headings:

- *rotational and vibrational energy transfer within and from Fermi resonance states in C_2H;*[10-12]

- *rate coefficients for rotational and vibrational energy transfer in collisions of $NO(X^2\Pi)$ with He, Ar, N_2 and NO at temperatures down to 7 K;*[13-15]

- *total and state-to-state relaxation from high rotational levels ($J \leq 40.5$) of $NO(X^2\Pi)$ in collisions with He, Ar and N_2.*[16]

Experimental Methods

Our general experimental method employs two tunable pulsed lasers. Pulses of IR radiation have been provided by one of two sources. The first is an optical parametric oscillator (OPO) in which tunable IR radiation is generated in a $LiNbO_3$ crystal pumped by the fundamental 1.064 µm output of a Nd:YAG laser. This device provides radiation between *ca* 1.4 and 3.5 µm in pulses of *ca.* 10 ns duration, an energy between 0.1 and 1.0 mJ, and a linewidth of *ca.* 0.25 cm^{-1}. It has been employed in the experiments described below in Section III(a) on energy transfer in acetylene, $C_2H_2(\tilde{X}^1\Sigma_g^+)$. Unfortuantely, the pulse-to-pulse stability from the OPO is poor.

For the experiments at ultra-low temperature (see Section III(b)) and on high rotational states of NO (Section III(c)), we were able to replace the OPO by a pulsed laser in which IR wavelengths were generated by difference frequency mixing the output of a Nd:YAG pumped dye laser with the fundamental wavelength of the pump laser. This source generated pulses of similar length to the OPO but much higher spectral brightness (5 mJ in *ca.* 0.1 cm^{-1}) and far superior pulse-to-pulse stability. It was used to excite $NO(X^2\Pi)$ from $v = 0$ to $v = 3$ (*ca.* 5544 cm^{-1}) in experiments at low temperature, and from $v = 0$ to $v = 2$ (*ca.* 3724 cm^{-1}) in experiments on NO in high rotational levels.

The evolution of the excited state population which was prepared using the IR pump laser was observed by performing LIF measurements using a frequency-doubled dye laser. In the course of this work, two different dye lasers have been used. In the room temperature experiments on acetylene and those on high rotational state of NO, the UV probe radiation was provided by frequency-doubling the output of a dye laser pumped by an excimer laser operating on XeCl at 308 nm. In the measurements of NO relaxation at ultra-low temperatures, the probe laser was also a frequency-doubled dye laser which, in this case, was pumped by a Nd:YAG laser operated at 355 nm.

Two kinds of experiments have been performed. In the first, referred to here as *kinetic* measurements, the frequencies of the IR pump and UV probe lasers were fixed, and the intensity of the LIF signal was measured as the time delay between the pulses provided by these two lasers was systematically varied. These experiments measured the evolution of population in a single rovibrational level, usually that which was populated directly by IR absorption. In the second type of experiment, which was *spectroscopic* in character, the delay between the two laser pulses was set to a particular value, usually corresponding to a fraction of the average time between collisions, and the frequency of the UV probe laser was scanned.

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The resultant spectrum could be analysed to determine populations in those levels populated in single collisions from the initially excited level. State-to-state rate coeffcients for rotationally inelastic collisions could then be derived from these populations.

The previous paragraphs describe the generic experiment. These methods have been implemented in three different environments to provide information about a number of different inelastic processes. Experiments on C_2H_2 have been performed in a simple room temperature cell. The IR pump laser excited molecules to a rotational level in a component state of one or other of two low-lying Fermi doublets in the $\tilde{X}^1\Sigma_g^+$ electronic ground state, either $(3_1/2_14_15_1)$ or $(3_14_1/2_14_25_1)$. LIF measurements were carried out via excitation to rovibrational levels in the $\tilde{A}^1A_u$ electronic state. The experiments on inelastic collisions involving $NO(X^2\Pi)$ in high rotational states were also carried out in a simple cell at room temperature. However, in these experiments, NO was prepared in a non-Boltmann distribution over internal energy states by photolysing NO_2 at 355 nm, using the frequency-tripled output of a Nd:YAG laser, and then some molecules were immediately promoted from a high rotational level in $v = 0$ to a high rotational level in $v = 2$ using the frequency-difference laser source as the IR pump.

The experiments on rotational and vibrational energy transfer in collisions involving $NO(X^2\Pi)$ at ultra-low temperatures were carried out in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus.[17] In this apparatus, which is only one of two of its kind world-wide, a supersonic flow of cold, relatively dense gas is formed by expansion through a convergent-divergent Laval nozzle. Before the work which is described here, this equipment and its French cousin[18] had only been used to measure the rate coefficients for elementary reactions of radicals (CN, OH and CH) with neutral molecules. In the present work, the double resonance method was implemented in the manner described above to provide information about energy transfer from and between rotational levels within the vibronic state $NO(X^2\Pi, \Omega = {}^3/_2, v = 3)$ in collisions with He, Ar and N_2, and about vibrational self-relaxation from this vibrational state in NO-NO collisions.

The lasers were controlled and the LIF signals gathered and processed using standard methods which are described in our papers on this and previous work.[1-7, 10-16]

Results and Discussion

(a) Rotational and Vibrational Energy Transfer within and from Fermi Resonance States in C_2H_2 [10-12]

In its spectroscopic and dynamical properties C_2H_2 serves as a valuable bridge between *diatomic* molelcules, with their well-separated vibrational levels and low rates of vibrational relaxation, and *polyatomic* molecules, with their high density of vibrational states and generally facile relaxation. We have exploited the IRUVDR method to examine both vibrational and rotational relaxation in this molecule. The vibrational levels in the $\tilde{X}^1\Sigma_g^+$ electronic ground state are strongly mixed as a result of Fermi resonance. This mixing sets in at relatively low levels of excitation and we have examined the collisional behaviour of C_2H_2 molecules promoted to rovibrational states of both the $(3_1/2_14_15_1)$[a] and the $(3_14_1/2_14_25_1)$ Fermi dyads in *kinetic* experiments. One result of the strongly mixed character of these states is to bestow on them both IR and UV strength; the IR activity arising from the $|3_1\rangle$ or $|3_14_1\rangle$ zero order states, whilst the presence of $|2_1\rangle$ and $|4_1\rangle$ excitation improves the Franck-Condon factors to the $\tilde{A}^1A_u$ excited electronic state which is strongly *trans*-bent and has a longer CC bond than the ground state.

We have examined *vibrational* relaxation of C_2H_2 in samples of pure C_2H_2 and in C_2H_2 diluted in N_2 and H_2. IR radiation from the OPO excited molecules of C_2H_2 to a component vibrational state of one of the Fermi dyads, and the UV probe laser was used to observe the evolution of population either in that state or in the other component state of the same Fermi dyad in *kinetic* experiments. Rate coefficients have been determined for two kinds of processes: (a) vibration-to-vibration (V-V) transfer *between* the two component states of the same Fermi dyad induced by C_2H_2, N_2 and H_2, and (b) vibrational relaxation *from* the coupled pair of Fermi dyad states in collisions with the same gases. Table 1 gives the rate coefficients for intradyad V-V transfer and for vibrational relaxation from the coupled states of the two dyads which have been obtained in the present work.

In addition, populations have been observed in the (4_25_1), (4_15_1) and (4_2) states of C_2H_2 during relaxation from the $(3_14_1/2_14_25_1)$ dyad and rate constants for self-relaxation from the

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[a] The notation is adopted whereby 3_1 denotes one quantum of excitation in the ν_3 normal mode. Thus $(3_1/2_14_15_1)$ denotes the Fermi dyad in which the principal contributions to the vibrational eigenstates are from the normal mode wavefunctions describing the zero order 3_1 fundamental and the $2_14_15_1$ combination states.

Table 1 Rate coefficients and collisional probabilities $(P)^a$ for intradyad transfer between (k_{id}) and vibrational relaxation from (k_{vr}) the $(3_1/2_14_15_1)$ and $(3_14_1/2_14_25_1)$ Fermi dyads in C_2H_2.

	k_{id}/cm³ molecule⁻¹ s⁻¹		k_{vr}/cm³ molecule⁻¹ s⁻¹	
	$(3_1/2_14_15_1)$	$(3_14_1/2_14_25_1)$	$(3_1/2_14_15_1)$	$(3_14_1/2_14_25_1)$
C_2H_2	$(2.1 \pm 0.2)^b \times 10^{-10}$	$(3.2 \pm 0.6) \times 10^{-11}$	$(1.0 \pm 0.1) \times 10^{-10}$	$(6.9 \pm 0.6) \times 10^{-11}$
	0.43	0.065	0.20	0.14
H_2	$(8.6 \pm 1.0) \times 10^{-11}$	$(1.4 \pm 0.1) \times 10^{-12}$	$(1.2 \pm 0.2) \times 10^{-11}$	$(1.6 \pm 0.1) \times 10^{-11}$
	0.12	0.0019	0.017	0.022
N_2	$(2.6 \pm 0.8) \times 10^{-11}$	$(9 \pm 4) \times 10^{-13}$	$(1.9 \pm 0.6) \times 10^{-12}$	$(7.3 \pm 1.6) \times 10^{-13}$
	0.070	0.002	0.005	0.0020

[a] referred to the following rate coefficients for collisions subject to a Lennard-Jones potential: C_2H_2-C_2H_2: 16.0 Torr⁻¹ µs⁻¹ (= 4.91 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹); C_2H_2-H_2: 23.5 Torr⁻¹ µs⁻¹ (= 7.21 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹); C_2H_2-N_2: 12.2 Torr⁻¹ µs⁻¹ (= 3.74 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹).

[b] errors are cited at the 2σ level including only random errors.

first two of these states have been derived: $k_{vr}(4_25_1) = (7.9 \pm 3.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $k_{vr}(2_14_1) = (2.9 \pm 0.6) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

The observed rates of intradyad V-V transfer have been examined in terms of the transition matrix element in which the wavefunctions of the two component states of the Fermi dyad are expressed as sums and differences of the zero order wavefunctions for $|3_1\rangle$ and $|2_14_15_1\rangle$. Given the rapidity of this process, at least in C_2H_2-C_2H_2 collisions, it is concluded that the two diagonal terms in the matrix element, i.e. $\langle 3_1 | V | 3_1 \rangle$ and $\langle 2_14_15_1 | V | 2_14_15_1 \rangle$, must have very different values. On the basis of a number of arguments, not least the magnitude of the cross-sections for transfer, it is tentatively concluded that it may be the long-range attractive part of the potential between the collision partners which induces transfer. The rapid self-relaxation of C_2H_2 from each pair of coupled dyad states almost certainly occurs by intermolecular V-V exchange, although it appears as if no single process is dominant, rather a number of V-V channels contribute to the overall relaxation process.

We have also examined *rotational* relaxation of C_2H_2 in samples of pure C_2H_2 and in C_2H_2 diluted in He, Ar and H_2. One purpose of these experiments was to determine state-to-state rate coefficients for rotational energy transfer in collisions with the noble gases, in order to compare the experimental results with those of (a) simple classical calculations treating the collision partners as 'hard objects', and (b) quantum scattering calculations on *ab* initio potential energy surfaces. Pulses of tunable IR radiation from the OPO excited molecules of C_2H_2 to the $J_i = 10$ level of the lower component state (II) of the $(3_1/2_1 4_1 5_1)_{II}$ Fermi dyad in the $\tilde{X}^1\Sigma_g^+$ electronic ground state and tunable UV radiation was used to record laser-induced spectra at short delays.

In this way, state-to-state rate coefficients for transfer from J_i to J_f were determined for two kinds of processes: (a) rotational energy transfer (RET) induced by collisions with C_2H_2, Ar, He and H_2 from $J_i = 10$ to other levels ($J_f = 2$-8, 12-20) within the same component (II) of the $(3_1/2_1 4_1 5_1)$ Fermi dyad, and (b) intradyad transfer in C_2H_2 - C_2H_2 collisions to specific levels ($J_f = 2$-14, 18) in the other component (I) of this Fermi dyad. Transfer from II to I is found to account for *ca.* 16% of the total relaxation from (II, $J_i = 10$). The distribution of state-to-state rate coefficients for RET becomes broader as the mass of the collision partner increases. Absolute values of the state-to-state rate coefficients are determined by scaling the results to the previously determined rate coefficients for rotational relaxation by the same collision partner. The experimental results for C_2H_2-He and C_2H_2-H_2 collisions are in quite good agreement with the results of calculations using a simple classical model and 'hard' interactions to describe the intermolecular forces. The results with Ar as the collision partner are less well reproduced, probably because of the neglect of the larger intermolecular attraction in this case. The experimental data are, however, in excellent agreement with the results of quantum scattering calculations performed on an *ab initio* surface.

(b) Rate Coefficients for Rotational and Vibrational Energy Transfer in Collisions of NO($X^2\Pi$) with He, Ar, N_2 and NO at Temperatures down to 7 K [13-15]

Implementing the IRUVDR method in the supercold environment provided by the CRESU apparatus, we have obtained very extensive results on the rotational and vibrational relaxation of NO at temperatures down to 7 K Rate coefficients of two kinds have been measured for *rotational* energy transfer in collisions between NO and He, Ar and N_2: (a) rate coefficients for *total* removal from specific states of NO($X^2\Pi_{1/2}$; $v = 3$: $J = 0.5$, 3.5 or 6.5) and (b) *state-to-state* rate coefficients for rotational energy transfer from these levels to specific final rotational states. Using different Laval nozzles, results have been obtained for three different collision

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partners and at several different temperatures: for He as collision partner, 295, 149, 63, 27, 15 and 7 K; for Ar, 139, 53, 44 and 27 K; and for N_2, 86 and 47 K.

The thermally averaged cross-sections for total removal of NO from levels $J = 0.5$, 3.5 or 6.5 in collisions with He are displayed in Fig. 1. These thermally averaged cross-sections for all collision partners show remarkably little variation, either with temperature or with initial rotational state.

Fig. 1. Thermally averaged cross-sections for total removal of NO from $X^2\Pi_{1/2}$; $v = 3$; $J = 0.5$, 3.5 and 6.5 in collisions with He: The filled circles show the results of the present experiments; the open circles the data of Islam et al.,[7] and the squares joined by the dashed lines the results of the theoretical calculations.
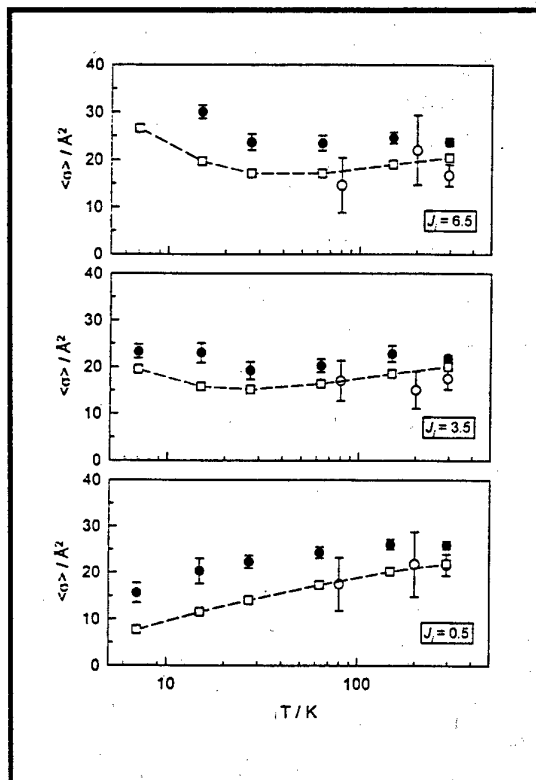
We have also determined a very large array of state-to-state rate coefficients for energy transfer from $J = 0.5$, 3.5 or 6.5 with He, Ar and N_2 at the temperatures specified above. Fig. 2 shows some representative data with He as the collision partner. The variation of state-to-state rate coefficients with ΔJ shows three general features: (i) a decrease with increasing ΔJ; (ii) a propensity to favour even ΔJ transitions over odd ΔJ changes; and (iii) at lower temperatures, decreases in J are increasingly favoured over increases in J and the distribution of rate coefficients against ΔJ becomes narrower.

Fig. 2. State-to-state rate coefficients for rotational energy transfer in: (a) NO-He collisions at 15 K, and (b) NO-He collisions at 149 K. The filled circles show the experimental results, the open circles joined by dotted lines the results of the theoretical calculations.
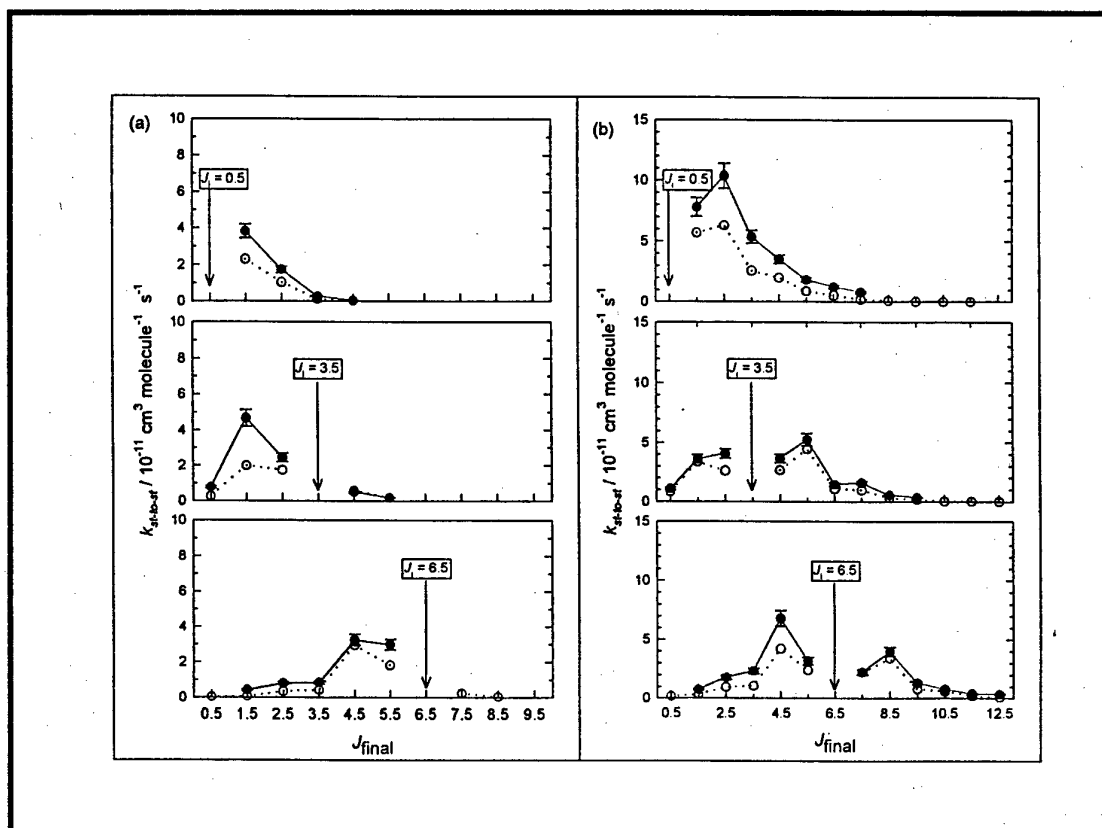
The experimental rate coefficients for total and state-to-state rotational energy transfer in collisions with He and Ar are compared in Figs. 1 and 2 with the results of close coupled and coupled states calculations (performed by Dr M. Yang and Professor M.H. Alexander) based on potential energy surfaces determined within the coupled electron pair approximation (CEPA) with a large atomic orbital basis set. The agreement between theory and experiment of both the total and the state-to-state rate coefficients is excellent over the complete range of temperatures covered in the experiments.

The results of these experiments and calculations on rotational energy transfer in $NO(X^2\Pi)$ have been the subject of two publications.[13,15] They represent the first such measurements at ultra-low temperatures and the most extensive and satisfactory comparison between experimental and theoretical results of this kind that have been obtained up to the present time.

We have also applied the IRUVDR technique in the CRESU apparatus to study the vibrational self-relaxation of NO(X$^2\Pi$, $v = 3$); *i.e.*

$$NO(v = 3) + NO(v = 0) \rightarrow NO(v < 3) + NO$$
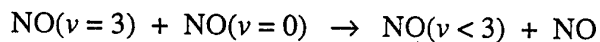
at temperatures between 58 K and 7 K.[14] Vibrational relaxation is found to be quite rapid and, as Fig. 3 shows, the rate coefficients are found to *increase* steeply as the temperature is lowered. The endothermicity of single quantum vibrational-vibrational (V-V) energy exchange ($\Delta E / hc = 55.9$ cm^{-1}) means that this process must become slow at the low temperatures of our experiments and cannot be responsible for the observed rates.

Fig. 3. Rate coefficients for self-relaxation of NO($v = 3$), compared with earlier data at higher temperatures (see ref. 14 for other work cited). The dashed line is a prediction of the rate coefficient based solely on V-V exchange.
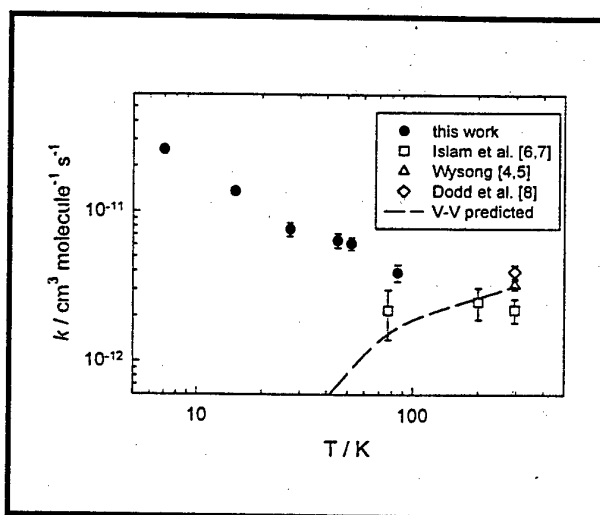
It is proposed that the fast relaxation which is observed must be due to vibrational-translational (V-T) energy transfer which is efficient because of the transient formation of (NO)$_2$ energised collision complexes in which intramolecular vibrational relaxation occurs at rates competitive with re-dissociation of the dimer to NO($v = 3$) + NO($v = 0$). This is a particularly interesting example of collisional relaxation being facilitated by the presence of strong attractive forces between the collision partners so that relatively long-lived collision complexes form. This subject has recently been reviewed by the Reporter.[19]

(c) Total and State-to-State Relaxation from High Rotational Levels ($J \leq 40.5$) of NO(X$^2\Pi$) in Collisions with He, Ar and N$_2$ [16]

A major objective in our programme in molecular energy transfer is to determine rate coefficients for total and for state-to-state energy transfer from high rotational levels. As

indicated earlier, we have devised a novel method whereby a species (in the present work, NO) is formed with a broad distribution over rotational levels by photodissociation of a suitable precursor. Before this non-Boltzmann distribution can relax, the IR pump laser is fired and promotes some sub-set of these molecules from a high rotational level in the ground vibrational state to an excited vibrational state and a level which is essentially unpopulated by the photolytic process. This procedure can be represented by the following equations:

laser 1: $NO_2 + hv\,(\lambda = 355\,nm) = NO(v, J) + O$

laser 2: $NO(v = 0, J) + hv\,(\lambda = 2.59\,\mu m) = NO(v = 2, J{+}1)$

laser 3: $NO(v = 2, J{+}1) + hv\,(\lambda = 247\,nm) = NO^*(A^2\Sigma^+\,v, J)$
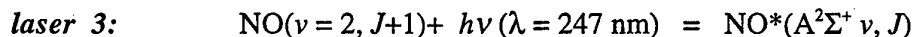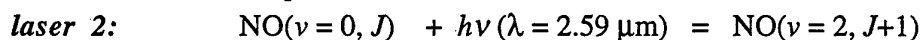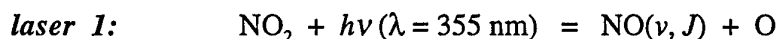
Fig. 4 shows some kinetic traces of LIF signal *versus* time which reflect the variation of population in $NO(X^2\Pi;\ \Omega = {}^3/_2;\ v = 2;\ J = 40.5)$ in mixtures of 10% NO in He. In Fig. 4, the first-order rate coefficients from experiments of this kind are plotted against the pressure of helium. The gradient yields the rate coefficients for total removal of NO from the specified level in collisions with He.

Fig. 4 Variation of LIF signals with time from $NO(X^2\Pi;\ \Omega = {}^3/_2; v = 2, J = 40.5)$

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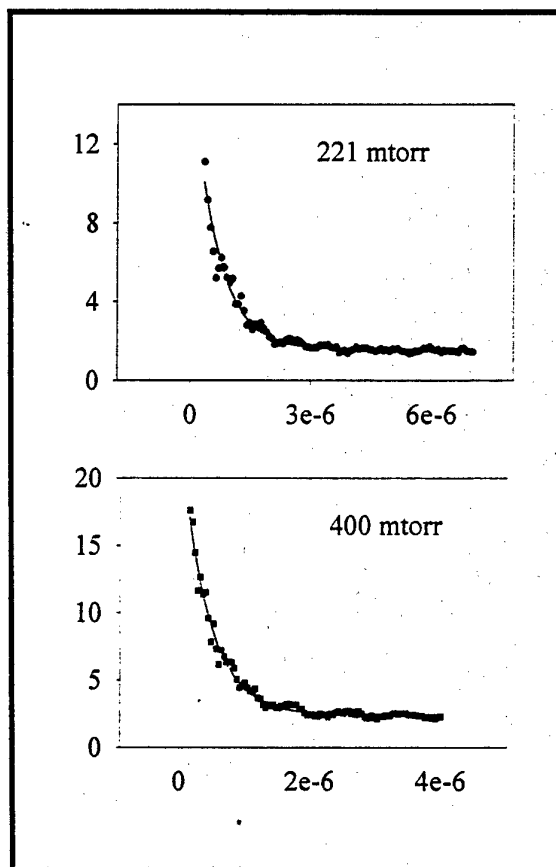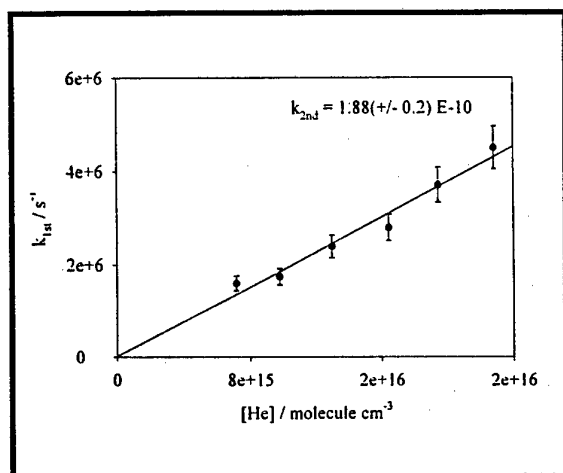
Fig. 5 First-order rate constants for relaxation of NO($X^2\Pi$; $\Omega = {}^3/_2$; $v = 2$, $J = 40.5$) plotted against the conentration of helium

Rate coefficients have been measured for both total and state-to-state energy transfer from four rotational level in $X^2\Pi$; $\Omega = {}^3/_2$; $v = 2$: $J_i = 7.5$, 20.5, 31.5 and 40.5. Experiments of the kind which have just been described, in which NO is formed by photolysis of NO_2 have been carried out for the last two of these levels; conventional IRUVDR experiments have been carried out on the first three of the levels. Rate coefficients for total removal from these four levels in collisions with Ar, He and N_2 are shown in Fig. 6.

Fig. 6 Rate coefficients for total removal of NO from $X^2\Pi$; $\Omega = {}^3/_2$; $v = 2$; J as a function of rotational level J

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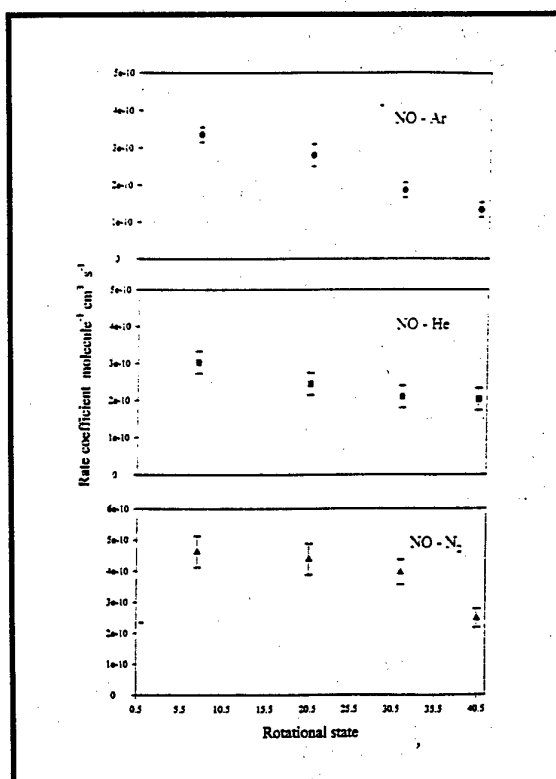
In the case of each collision partner, the rate coefficients show a relatively small but significant decrease with the value of the rotational quantum number.[20] This observation is line with what has been seen in line-broadening parameters, providing another piece of evidence for the correlation between these two phenomena. The least strong variation is found for helium as collision partner. This may be associated with the fact that the average velocity for NO-He collisions is a factor of 2.2 greater than in NO-Ar collisions and 2.0 greater than in those between NO and N_2. As a consequence, collisions of the last two kinds are appreciably less 'sudden' and they appreciate a more rotationally averaged potential, since the rotational period of the molecule in high J levels is comparable to the characteristic time of the collision.

In addition we have measured state-to-state rate coefficients for all combinations of initial rotational level (J_i = 7.5, 20.5, 31.5 and 40.5) and collision partner (He, Ar and N_2). Examples of the results are shown in Fig. 7.

Fig. 7 State-to-state rate coefficients for energy transfer from J_i = 7.5, 20.5 and 31.5 in NO($X^2\Pi$; $\Omega = ^3/_2$; v = 2)in collisions with He..

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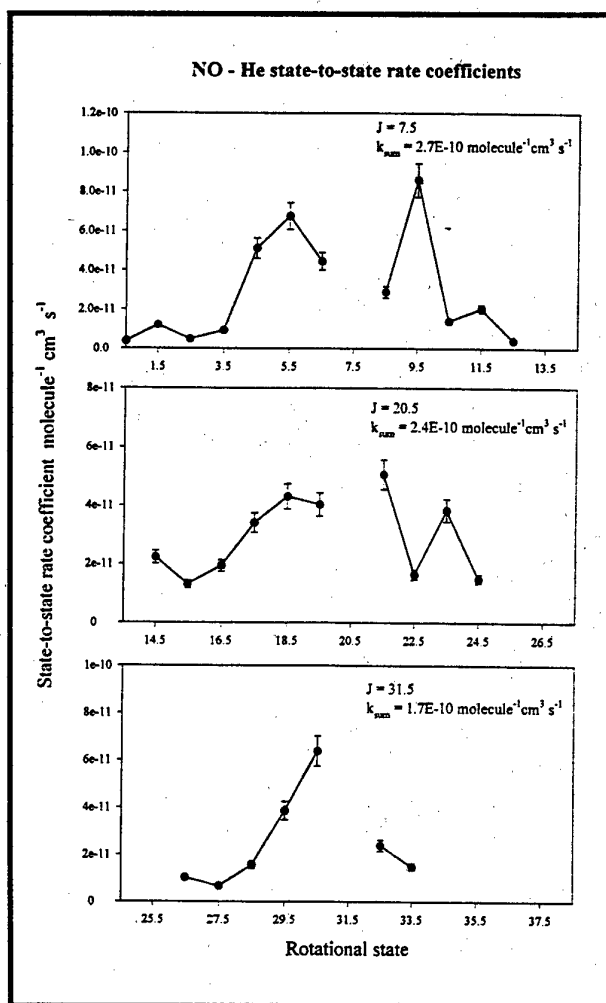
The state-to state rate coefficients for rotational energy transfer show a clear propensity to be dominated by smaller ΔJ changes as J_i increase. This is accentuated for the highest value of J_i studied in the present work; i.e. $J_i = 40.5$. For this initial level, for which state-to-state data are not shown, remarkably over 80% of the transfer occurs to $J = 39.5$. These recent experimental results will be compared with the results of *ab initio* calculations in the near future.

Future Research

Our future research in the area of molecular energy transfer will have three interrelated strands, based on the work which has been summarised in this report. First, to understand further the factors which control vibrational energy transfer in polyatomic molecules where the vibrational states, even at low levels of excitation, can be expressed as mixtures of zero order normal mode states, we shall perform measurements on isotopomers of C_2H_2, initially C_2HD. Because the energies associated with the normal mode states, as well as the nature of the vibrations, change appreciably from C_2H_2 to C_2HD, the strength of any Fermi resonances is altered considerably. Thus, in C_2HD the highest fundamental vibration, the C-H stretch, is a relatively pure normal mode. Using double resonance and/or laser-induced vibrational fluorescence methods, we shall measure rate coefficients for relaxation from this level in collisions with both C_2H_2 and the noble gases.

The second project will be to extend our low temperature measurements on rotational energy transfer to molecules of more direct astrophysical interest than NO. Such rate coefficients are required to interpret measurements of the observed line intensities from astrophysical sources, especially dense interstellar clouds. These observations are employed to derive the temperature and molecular abundances in such clouds and are therefore an essential component in understanding the chemistry and physics in these vast regions of the interstellar medium.

Finally, and of most relevance to the original objectives of the proposal to AFOSR, we shall continue our work on high rotational levels of diatomic species. Our measurements on NO are complete. During the period of future loans of the frequency-difference IR laser, we shall extend our experiments to OH and CN. These are somewhat more demanding than those on NO. Since OH and CN are inherently unstable, it makes it more difficult to carry out the necessary preliminary spectroscopic experiments. Nevertheless, there is every reason to suppose that measurements of rate coefficients for total and state-to-state rotational energy transfer in collisions of OH and CN with inert collision partners are possible. In addition, we intend to examine the kinetics of CN radicals with molecules, such as C_2H_2, with which the

radicals undergo rapid reaction. In these instances, it should be possible to determine the relative rates of reaction and energy transfer for individual J_1 and to determine rate coefficients for reaction for different initial rotational levels.

References

[1] I.W.M. Smith and J.F. Warr, Tunable IR - Tunable UV Double Resonance Experiments on HCN, *J. Chem. Soc., Faraday Trans.*, **1991**, *87*, 205.

[2] M.J. Frost and I.W.M. Smith, Infrared-Ultraviolet Double Resonance Measurements on the Relaxation of Rotational Energy in the $(3_1,2_14_11_1)$ Fermi Resonance States of C_2H_2, *Chem. Phys. Letters*, **1992**, *191*, 574.

[3] M.J. Frost. Energy Transfer in the $3_1,2_14_15_1$ Fermi-Resonant States of Acetylene. I. Rotational Energy Transfer, *J. Chem. Phys.*, **1993**, *98*, 8572.

[4] M. J. Frost and I. W. M. Smith, Energy Transfer in the $3_1,2_14_15_1$ Fermi-Resonant States of Acetylene. II. Vibrational Energy Transfer, *J. Phys. Chem.* **1995**, 99, 1094.

[5] M.J. Frost, M. Islam and I.W.M. Smith, Infrared-Ultraviolet Double Resonance Measurements on the Temperature Dependence of Rotational and Vibrational Self-Relaxation of NO $(X^2\Pi,v=2,j)$,*Can. J. Chem.*, **1994**, *72*, 606.

[6] M. Islam, I.W.M. Smith and J.W. Wiebrecht, Infrared-Ultraviolet Double Resonance Measurements on the Temperature-Dependence of Relaxation from Specific Rovibronic Levels in NO$(X^2\Pi, v=2,j)$ and $(X^2\Pi, v=3,j)$, *J. Phys. Chem.*, **1994**, *98*, 9285.

[7] M. Islam, I.W.M. Smith and J.W. Wiebrecht, Infrared-Ultraviolet Double Resonance Measurements on the Rate Constants for Collisionally-Induced State-to-State R, 9676.otational and Spin-Orbit Energy Transfer in NO $(X^2\Pi, v = 2)$, *J. Chem. Phys.*, **1995**, *103*

8   J.A. Dodd, S.J. Lipson, J.R. Lowell, P.S. Armstrong, W.A.M. Blumberg, R.M. Nadile, S.M. Adler-Golden, W.J. Marinelli, K.W. Holtzclaw and B.D. Green, Analysis of Hydroxyl Earthlimb Airglow Emissions: Kinetic Model for State-to-State Dynamics of OH (v,N) (), *J. Geophys. Res.*, **1994**, *99*, 3559.

9   P.S. Armstrong, S.J. Lipson, J.A. Dodd, J.R. Lowell, W.A.M. Blumberg and R.M. Nadile, Highly Rotationally Excited NO(v, J) in Thermosphere from CIRRIS 1A Limb Radiance Measurements, *Geophys. Res. Lett.*, **1994**, *21*, 2425.

10 S. Henton, M. Islam and I.W.M. Smith, Intramolecular V-V Transfer between the Components of the $(3_1/2_14_15_1)$ and $(3_14_1/2_14_25_1)$ Fermi Dyads in Acetylene in C_2H_2- C_2H_2 Collisions, *Chem. Phys. Letters*, **1998**, in press.

11 S. Henton, M. Islam and I.W.M. Smith, Relaxation within and from the $(3_1/2_14_15_1)$ and $(3_14_1/2_14_25_1)$ Fermi Dyads in Acetylene: Part I - Vibrational Relaxation in Collisions with C_2H_2, N_2 and H_2, *J. Chem. Soc. Faraday Trans.*, **1998**, submitted.

12 S. Henton, M. Islam and I.W.M. Smith, Relaxation within and from the $(3_1/2_14_15_1)$ and $(3_14_1/2_14_25_1)$ Fermi Dyads in Acetylene: Part II - Rotational Energy Transfer in Collisions with C_2H_2, Ar, He and H_2, *J. Chem. Soc. Faraday Trans.*, **1998**, submitted.

13 P.L. James, I.R. Sims and I.W.M. Smith, Total and State-to-State Rate Coefficients for Rotational Energy Transfer in Collisions between $NO(X^2\Pi)$ and He at Temperatures down to 15 K, *Chem. Phys. Letters*, **1997**, *272*, 412.

14 P.L. James, I.R. Sims and I.W.M. Smith, Rate Coefficients for the Vibrational Self-Relaxation of $NO(X^2\Pi, v = 3)$ at Temperatures down to 7 K, *Chem. Phys. Letters*, **1997** *276*, 423.

15 P.L. James, I.R. Sims, I.W.M. Smith, M.H. Alexander and M. Yang, A Combined Experimental and Theoretical Study of Rotational Energy Transfer in Collisions between $NO(X^2\Pi_{1/2}; v = 3, J)$ and He, Ar and N_2 at Temperatures down to 7 K, *J. Chem. Phys.*, **1998** in press.

16 M. Islam and I.W.M. Smith, two papers in preparation

[17] I.R. Sims and I.W.M. Smith, Gas-Phase Reactions and Energy Transfer at Very Low Temperatures, *Ann. Rev. Phys. Chem.*, **1995**,*46*, 109.

[18] I.R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe and I.W.M. Smith, Ultra-Low Temperature Kinetics of Neutral-Neutral Reactions: The Technique, and Results for the Reactions $CN + O_2$ down to 13 K and $CN + NH_3$ down to 25 K, *J. Chem. Phys.*, **1994**, *100*, 4229.

[19] I.W.M. Smith, Collisional Energy Transfer, Intramolecular Vibrational Relaxation and Unimolecular Reactions, *J. Chem. Soc. Faraday Trans.* (Feature Article), **1997**, *93*, 3741.

[20] (a) A.S. Pine, A.G. Maki and N.-Y. Chou, *J. Mol. Spectrosc.* **1985**, *114*, 132; (b) A.S. Pine, Photoacoustic Measurement of Differntial Broadening of the doublets of $NO(X^2\Pi_{1/2}; v = 2 - 0)$ by Ar, *Chem. Phys.* **1989**, *91*, 2002.

[17] I.R. Sims and I.W.M. Smith, Gas-Phase Reactions and Energy Transfer at Very Low Temperatures, *Ann. Rev. Phys. Chem.*, **1995,**46, 109.

[18] I.R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe and I.W.M. Smith, Ultra-Low Temperature Kinetics of Neutral-Neutral Reactions: The Technique, and Results for the Reactions $CN + O_2$ down to 13 K and $CN + NH_3$ down to 25 K, *J. Chem. Phys.*, **1994**, *100*, 4229.

[19] I.W.M. Smith, Collisional Energy Transfer, Intramolecular Vibrational Relaxation and Unimolecular Reactions, *J. Chem. Soc. Faraday Trans.* (Feature Article), **1997**, *93*, 3741.

[20] (a) A.S. Pine, A.G. Maki and N.-Y. Chou, Pressure Broadening, Lineshapes, and Intensity Measurements in the 2 - 0 Band of NO, *J. Mol. Spectrosc.* **1985**, *114*, 132; (b) A.S. Pine, Photoacoustic Measurement of Differential Broadening of the doublets of $NO(X^2\Pi_{1/2}; v = 2 - 0)$ by Ar, *Chem. Phys.* **1989**, *91*, 2002.

CHEMICAL PHYSICS LETTERS

Rate coefficients for the vibrational self-relaxation of NO(X $^2\Pi$, $v = 3$) at temperatures down to 7 K

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Abstract

Infrared–ultraviolet double resonance (IRUVDR) experiments have been implemented in the super-cold environment provided by a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. This method has enabled us to measure rate coefficients for the vibrational self-relaxation of NO(X $^2\Pi$; $v = 3$), i.e. NO($v = 3$) + NO → NO($v < 3$) + NO. Using different Laval nozzles, results have been obtained at six different temperatures between 85 and 7 K. The rate coefficients *increase* strongly as the temperature is lowered. The endothermicity of single quantum vibrational–vibrational (V–V) energy exchange ($\Delta E/hc = 55.9$ cm^{-1}) means that the rate of this process must *decrease* markedly at the lowest temperatures of our experiments. Therefore, the high relaxation rates which are observed must be due to vibrational–translational (V–T) energy transfer. It is proposed that this process is efficient because of the transient formation of $(NO)_2$ collision complexes in which intramolecular vibrational energy transfer occurs at rates competitive with re-dissociation of the dimer to NO($v = 3$) and NO($v = 0$). © 1997 Elsevier Science B.V.

1. Introduction

The collisionally-induced relaxation of NO from excited vibrational levels of its X $^2\Pi$ electronic ground state has been a subject of interest for many years. With most *molecular* collision partners, the dominant relaxation mechanism is single quantum vibrational–vibrational (V–V) energy exchange. This is also true for *self-relaxation* of NO vibrational levels above $v = 1$ [1–8], when the V–V process can be represented by the equation:

$$NO(v) + NO(v = 0) \to NO(v - 1) + NO(v = 1) \tag{1}$$
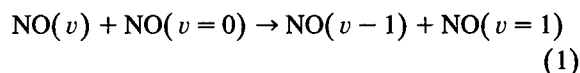
When relaxation is dominated by V–V energy exchange, NO appears to behave as a "normal", non-hydride, diatomic molecule; that is, there is no clear

evidence that its rate of relaxation is affected by the fact that the electronic ground state is $^2\Pi$ rather than $^1\Sigma$. Thus the rates of processes represented by Eq. (1) are similar to those for self-relaxation of CO from high vibrational levels [9–11].

The situation is different for self-relaxation of NO($v = 1$) which must occur by vibrational–translational (V–T) energy transfer. At room temperature, this process

$$NO(v = 1) + NO(v = 0) \to 2NO(v = 0) \tag{2}$$
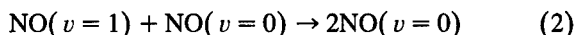
is much faster [12–16] than the corresponding processes for CO($v = 1$) [17,18]. At 300 K, the rate constant for Eq. (2) is $k(v = 1) = 7.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [12–16], a result which compares with $k(v = 1) < 10^{-20}$ cm^3 molecule^{-1} s^{-1} for the corresponding self-relaxation process in CO [17,18].

Moreover, the temperature dependence of $k(v = 1)$ is quite different in the two cases. For CO, the rate constant for self-relaxation above room temperature shows a strong positive dependence on temperature, approximately in accord with the predictions of SSH (Schwartz, Slawsky and Herzfeld) theory [19,20], whereas for NO the variation of $k(v = 1)$ shows a shallow minimum at around room temperature [14].

The unusually rapid V–T relaxation of $NO(v = 1)$ has attracted considerable theoretical attention. The early experimental observations led to the proposal by Nikitin [21] that V–T relaxation occurs by an electronically non-adiabatic mechanism. That is, during collisions, the system undergoes a transition between different vibronic states at geometries where the energy splitting between different electronic potential energy surfaces matches the separation of the $(v = 1)$ and $(v = 0)$ vibrational levels. An alternative possibility in the case of NO–NO collisions is that relaxation is facilitated by the nature of the lowest potential energy surface. It is known that NO can form $(NO)_2$ dimers which are held together by a bond that is weak $(D_0 = 8.5$ kJ mol$^{-1} \equiv 710$ cm^{-1} [22–25]), but which is stronger and more directional than van der Waals attraction, and it has been suggested [22–27] that this attraction, like that between species that can form hydrogen bonds, might accelerate energy transfer.

Weak intermolecular attractions are likely to exert their greatest effect on collisional processes at low temperatures, when the average kinetic energy is much less than the well-depth on the intermolecular potential. The lowest temperature at which self-relaxation in NO had been investigated before the present work was 77 K, in the experiments performed in cryogenically cooled cells on the relaxation of $NO(v = 2)$ and $NO(v = 3)$ by Islam et al. [6,7]. Earlier, Stephenson [12,13] had measured the rate of self-relaxation of $NO(v = 1)$ at 100 K. In the present paper, rate constants for vibrational self-relaxation of $NO(v = 3)$ are reported at temperatures down to 7 K. These data have been obtained by implementing the IRUVDR (Infrared–Ultraviolet Double Resonance) technique in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus [28,29]. We have previously reported the results of such experiments yielding total and state-to-state rate coefficients for rotational energy transfer in collisions between NO and He at temperatures down to 15 K [29].

2. Experimental method

Our experiments make use of a CRESU apparatus which has recently been established in Birmingham, and, in other respects, they are similar to those that have been performed previously in our laboratory to measure total and state-to-state rate coefficients for rotational energy transfer in collisions between NO and He [6,7,29]. Pulses of tuneable infrared radiation at ca. 1.8 μm were provided by difference frequency mixing. An injection-seeded Nd:YAG laser (Continuum Powerlite 8010) provided frequency-doubled pump radiation at 532 nm for a dye laser (Continuum ND6000) operating at ca. 670 nm on a mixture of DCM and LD700 dyes (Exciton) in methanol. The dye laser beam was then combined with residual narrow band 1064 nm radiation from the injection-seeded Nd:YAG laser in a LiNbO$_3$ crystal mounted within an autotracking unit (Continuum), to give the difference frequency radiation at ca. 1.8 μm. Typically, pulse energies of 5 mJ and spectral bandwidths of 0.1 cm^{-1} were achieved, though it is estimated that only ca. 1–2 mJ reached the experiment. The IR frequency was initially chosen by reference to signals from a photoacoustic cell filled with 10 Torr NO, though once the technique had been established, double-resonance LIF was used to tune the IR. The population in the $v = 3$ level of the $X\,^2\Pi_{1/2}$ state was observed by exciting LIF in the (0,3) band of the $(A\,^2\Sigma^+-X\,^2\Pi)$ system using the frequency-doubled output of a second dye laser (LAS LDL205) pumped by the frequency-tripled output of another Nd:YAG laser (Spectron SL805), and operating on Coumarin 500 laser dye (Exciton) in methanol. The two laser beams were combined and co-propagated through the gas reservoir and nozzle in the CRESU apparatus and along the axis of the supersonic flow downstream from the nozzle.

The Birmingham CRESU apparatus closely resembles the one in Rennes which has been used to measure rate constants for elementary neutral–neutral reactions and which has been described fully elsewhere [28]. The six nozzles used in the present work were characterised by impact-pressure measurements which yielded temperatures of 85, 52, 45

27, 15 and 7 K. In some cases, these temperatures were confirmed by recording LIF spectra of NO at a time delay of 5 μs which was long enough to allow complete equilibration of the rotational state distribution but short enough for vibrational relaxation to be prevented. To achieve 7 K, the gas reservoir and the nozzle itself were cooled by liquid N_2.

The IR-pump laser in our experiments causes initial excitation to a single rotational level in the $v = 3$ vibrational level of the lower spin–orbit component ($\Omega = 1/2$) of the $^2\Pi$ electronic ground state of NO. Our previous experiments [29] and those of Islam et al. [6,7] on rotational energy transfer demonstrated that, as a result of collisions between NO and the carrier gas, rotational and spin–orbit relaxation would be complete within ca. 2 μs in all the gas flows used in the present work. On the other hand, helium, argon and nitrogen are all inefficient at inducing vibrational relaxation [12,13]. Consequently, the rate coefficient for self-relaxation of NO($v = 3$) at each temperature could be determined by performing a series of experiments on gas flows which contained different concentrations of NO. For each gas mixture (the mole fraction of NO was, in all cases, < 2%), the first-order decay of LIF signal from NO($v = 3$) was measured as the time delay between the IR-pump laser and the UV-probe laser was varied systematically. In the case of experiments at 7 K, the amount of NO included in the gas mixture was limited to 0.1% by the requirement not to exceed the vapour pressure of NO at 77 K (81 mTorr) in the liquid N_2 cooled gas reservoir prior to expansion through the Laval nozzle.

3. Results

Typical traces of LIF signal plotted versus the time delay between pulses from the pump and probe lasers are displayed in Fig. 1. It is evident that the signals did not in all cases fully return to their pre-trigger value during the time it took for the supersonic gas flow to travel the distance from the exit of the Laval nozzle to the downstream observation point [28]. The values of the pseudo-first-order decay coefficients that could be obtained were limited (a) by the magnitude of the second-order rate coefficient for self-relaxation and (b) by the amount
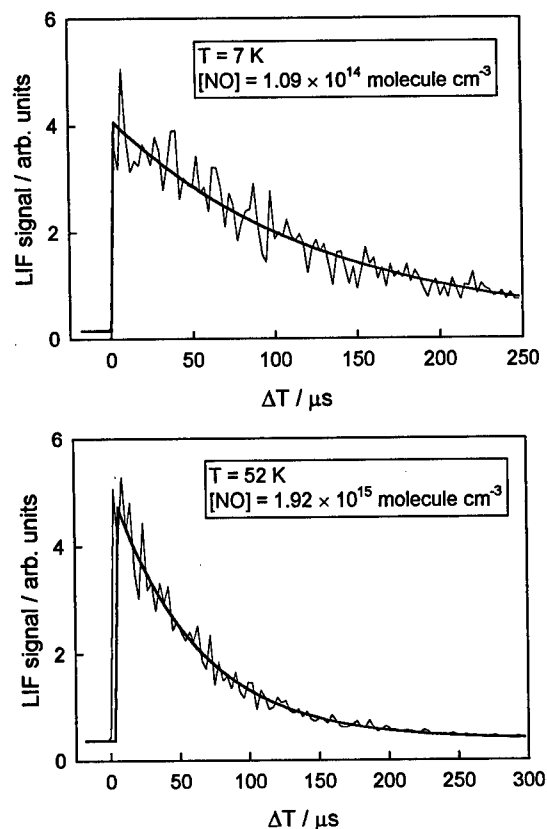

Fig. 1. Traces showing the variation of LIF signal with time delay ΔT between the IR-pump and UV-probe lasers at 7 K and 52 K, with the concentration of NO indicated. The results of non-linear least square fits to a single exponential decay are also shown.

of NO that can be included in the gas flow. In experiments at 7 K, where the gas was pre-cooled by liquid N_2 prior to expansion through the Laval nozzle, the NO concentration was restricted by its vapour pressure at 77 K (see above). In the other experiments, the amount of NO was kept below 2% of the total gas to maintain the integrity and uniformity of the supersonic gas flow.

A non-linear least-squares algorithm was employed to fit each trace of LIF intensity versus time delay to a single exponential decay, yielding pseudo-first-order rate coefficients, k_{1st}, for vibrational relaxation. Fitting was started after a delay of 5 μs to ensure complete rotational and spin–orbit relaxation, and the baseline was fixed using points recorded with "negative" time delays (probe before
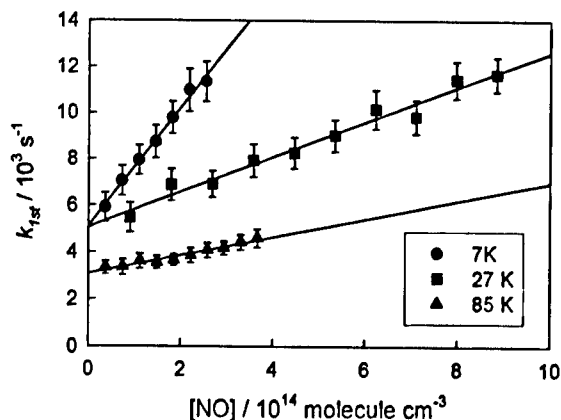
Fig. 2. Variation of first-order rate coefficients, k_{1st}, for self-relaxation of NO($v = 3$) with concentration of NO, [NO], at 7 K, 27 K and 85 K.

pump), necessitated by the restricted scan times arising in some cases from the finite duration of the uniform supersonic flow. The set of first-order rate coefficients obtained at a given temperature was then plotted against the concentration of NO present in the flowing gas mixture as shown in Fig. 2. The gradients of the lines gave the second-order rate coefficients (k) for self-relaxation of NO($v = 3$) which are listed in Table 1. The intercepts obtained from these plots were consistent with the rate estimated for diffusion out of the volume illuminated by both the pump and the probe lasers. The linear dependence of k_{1st} versus [NO] in all cases demonstrates the absence of any stable $(NO)_2$ dimer formation under these conditions. The last column of Table

Table 1

Rate coefficients, k, and thermally-averaged cross-sections, S, for vibrational self-relaxation of NO($v = 3$) in the temperature range $T = 7$–85 K. The nature of the carrier gas, M, and its total density are also indicated for each measurement

T (K)	[M] (10^{16} molecule cm^{-3})	M	k (10^{-12} cm^3 molecule^{-1} s^{-1})	$\langle S \rangle$ (Å^2)
7	19.2	He	25.8±1.8	26.0±0.2 [a]
15	5.05	He	13.6±0.6	9.35±0.40
27	4.53	He	7.6±0.8	3.87±0.42
45	2.92	Ar	6.4±0.7	2.55±0.26
52	5.36	Ar	6.1±0.6	2.27±0.24
85	1.69	N$_2$	3.9±0.5	1.12±0.15

[a] All errors quoted are ±$t\sigma$ statistical error where t is the appropriate value of Student's t-distribution for the 95% point.

1 lists the thermally averaged cross-section for vibrational self-relaxation calculated by dividing the second-order rate coefficient by the mean relative speed in NO–NO collisions at that temperature.

4. Discussion

The rate coefficients for vibrational self-relaxation of NO($v = 3$) which have been obtained in the present work at very low temperatures are compared in Fig. 3 with those from previous studies conducted at and above 77 K. Where they overlap with the result of Islam et al [6,7] at 77 K, the present results are ca. 80% higher. The reason for this discrepancy is unknown, although we note that the rate coefficient measured at 295 K by Islam et al. is also somewhat lower than other recently measured values [4,5,8].

Below 77 K, where the present results are quite unique, the rate coefficients for vibrational self-relaxation of NO($v = 3$) are large and show a strong negative temperature dependence. The relatively rapid self-relaxation of NO($v > 1$) at $T \geq 77$ K has been ascribed to near-resonant V–V energy exchange [4–7]. However, because of vibrational anharmonicity, this process, which is represented by Eq. (1) with $v = 3$, is endothermic by 55.9 cm^{-1}, which corresponds to a value of $\Delta E/k_B$ (where k_B is the Boltzmann constant) of 80 K. Consequently,
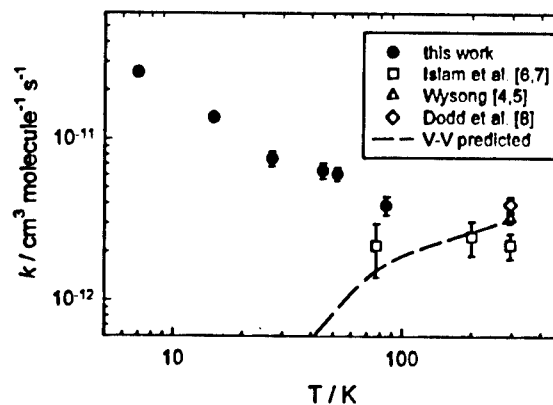

Fig. 3. Variation of rate coefficients for self-relaxation of NO($v = 3$) with temperature presented on a log–log plot, showing results from the present work, and for comparison, results from Islam et al. [6,7], Wysong [4,5] and Dodd et al. [8]. The dashed line is a prediction of the rate coefficient based solely on (V–V) exchange, as described in the text.

the rate of V–V energy exchange between $NO(v = 3)$ and $NO(v = 0)$ must decrease sharply through the temperature range covered by our experiments. The dashed line in Fig. 3 is a rough estimate of its rate constant, based on the assumption that the rate constant for the reverse exothermic process, i.e. V–V energy exchange between $NO(v = 2)$ and $NO(v = 1)$, is invariant with temperature and equal to the average of the values determined at room temperature by Wysong [4,5], Islam et al. [6,7] and Dodd et al. [8]. Stephenson [13] finds a value for the rate coefficient for relaxation of $NO(v = 1)$ by NO (which can only occur by V–T transfer) at room temperature which is ca. 40 times less than this average value for $NO(v = 3)$ relaxation by NO. While a small increase in V–T energy transfer rate would be expected in passing from $NO(v = 1)$ to $NO(v = 3)$, most of the relaxation rate for $NO(v = 3)$ at room temperature must therefore be as a result of V–V transfer. However, it is clear from Fig. 3 that V–V energy exchange cannot be responsible for the rapidly accelerating rate of self-relaxation of $NO(v = 3)$ which we observe as the temperature is lowered towards 0 K.

If V–V energy exchange is excluded, then the observed rates of relaxation must correspond to those for V–T energy transfer and it seems certain that the rapidity of this process must be associated with the relatively strong attractive forces which lead to formation of $(NO)_2$ dimers at low temperatures [22–25]. At 7 K, the lowest temperature of our experiments, $D_0/k_B T$ [22–25] is equal to ca. 150, and it seems likely that transient collision complexes can form in collisions between $NO(v = 3)$ and $NO(v = 0)$, with lifetimes with respect to re-dissociation that are long enough for intramolecular vibrational relaxation, and hence vibrational predissociation, to occur. This mechanism for facile, collisionally-induced, vibrational relaxation has previously been invoked [30,31] to explain the rapid rates found for relaxation of one radical species by another (e.g. $NO(v = 1)$ by radical atoms [32,33] and $OH(v = 1)$ by NO and NO_2 [34]). Unfortunately, and contrary to the situation for radical–radical systems [30,31], there have been no measurements of the pressure-dependent rates of association of two NO molecules to form $(NO)_2$. It is therefore impossible to compare the present results with rate coefficients for association to the dimer in the limit of high pressure.

The phenomenon of vibrational predissociation of $(NO)_2$ dimers has been investigated in a series of elegant experiments by Casassa et al. [22–25]. They created dimers in free jet expansions of NO and excited them to various vibrationally excited states using tuneable infrared radiation. The rates of vibrational predissociation were found to depend quite strongly on which vibration was excited. Thus, the dimer with one quantum in the *symmetric* NO stretch mode was found to have a mean lifetime of 880 ps, whereas for the dimer with one quantum in the *anti-symmetric* NO stretch vibration the lifetime with respect to vibrational predissociation is only 39 ps [24]. It is not clear which value provides the better estimate of the rate of intramolecular energy transfer in $(NO)_2$ complexes formed at low temperatures from association of $NO(v = 3)$ with $NO(v = 0)$.

Casassa et al. [24,25] have discussed the mechanism for vibrational predissociation of $(NO)_2$ dimers in some detail. They pointed out that eight electronic potential energy surfaces, four singlets and four triplets, correlate with $NO(X\,^2\Pi_\Omega) + NO(X\,^2\Pi_\Omega)$ and they discussed whether the mechanism for dissociation of a dimer which is excited vibrationally in one or both of the monomer units involves intramolecular vibrational energy transfer within the $^1A'$ electronic ground state or an electronically non-adiabatic mechanism in which the dimer dissociates via an electronically excited state. Unfortunately, although the electronic and geometric structure of the $(NO)_2$ $^1A'$ ground state are well-characterised, little is known about the excited states.

Since the spin–orbit splitting in the electronic ground state of NO is 121 cm^{-1}, corresponding to $(\Delta E_{s-o}/k_B) = 174$ K, in our experiments at temperatures ≤ 85 K only the lower $\Omega = 1/2$ spin–orbit component is appreciably populated, reducing to two (one singlet and one triplet) the number of surfaces which can be accessed adiabatically. If one assumes that only one quarter of NO + NO collisions occur on the $^1A'$ potential energy surface and that only these collisions cause vibrational relaxation, then our values of k_{relax} correspond to thermally averaged cross-sections for relaxation on this surface of 33 Å^2 at 15 K and 103 Å^2 at 7 K.

To examine whether these cross-sections correspond to relaxation in every collision on the $^1A'$ ground electronic surface, we compare them with the

cross-sections, $\langle S \rangle_{\mathrm{LJ}}$, determined for capture on an orientation-averaged Lennard–Jones potential. Then, according to a simple two-body model, $\langle S \rangle_{\mathrm{LJ}} = \pi \sigma_{\mathrm{LJ}}^2 \Omega^{(2,2)^*}$, where $\Omega^{(2,2)^*}$ is the collision integral [35]. With values of the Lennard–Jones parameters of $\sigma_{\mathrm{LJ}} = 3.49$ Å and $\varepsilon_{\mathrm{LJ}}/k_{\mathrm{B}} = 117$ K, the values of $\langle S \rangle_{\mathrm{LJ}}$ are ca. 200 Å^2 at 15 K and 260 Å^2 at 7 K. It therefore appears that, even at the lowest temperatures of our experiments, vibrational relaxation may not occur in every collision on the lowest $(NO)_2$ potential in which capture occurs, but that re-dissociation of the complexes to $NO(v = 3) + NO(v = 0)$ prior to vibrational predissociation may occur in a fraction of these collisions.

5. Summary

Implementing an infrared–ultraviolet double resonance technique within the extremely cold environment provided by expansion through a Laval nozzle in a CRESU apparatus, rate coefficients have been measured for the vibrational relaxation of $NO(v = 3)$ in collisions with $NO(v = 0)$ at six temperatures between 85 and 7 K. The rate coefficients show a marked negative dependence on temperature, reaching a value at 7 K which suggests a collisional deactivation efficiency approaching unity. It is pointed out that the observed relaxation must be the result of V–T energy transfer, since V–V energy exchange is too endothermic to occur at the rates which are observed experimentally at the lowest temperatures. It is further proposed that V–T energy transfer is facilitated by the transient formation of $(NO)_2$ complexes which last long enough for vibrational predissociation within the complexes to compete with re-dissociation to $NO(v = 3) + NO(v = 0)$.

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References

[1] H. Horiguchi, S. Tsuchiya, Jpn. J. Appl. Phys. 18 (1979) 1207.

[2] R.G. Macdonald, F.C. Sopchyshyn, Chem. Phys. 94 (1985) 455.

[3] X. Yang, E.H. Kim, A.M. Wodtke, J. Chem. Phys. 96 (1992) 5111.

[4] I.J. Wysong, Chem. Phys. Lett. 227 (1994) 69.

[5] I.J. Wysong, J. Chem. Phys. 101 (1994) 2800.

[6] M.J. Frost, M. Islam, I.W.M. Smith, Can. J. Chem. 72 (1994) 606.

[7] M. Islam, I.W.M. Smith, J.W. Wiebrecht, J. Phys. Chem. 98 (1994) 9285.

[8] J.A. Dodd, S.M. Singleton, S.M. Miller, P.S. Armstrong, W.A.M. Blumberg, Chem. Phys. Lett. 260 (1996) 103.

[9] G. Hancock, I.W.M. Smith, Appl. Opt. 10 (1971) 1827.

[10] I.W.M. Smith, C. Wittig, J. Chem. Soc. Faraday Trans. 269 (1973) 939.

[11] H.T. Powell, J. Chem. Phys. 59 (1973) 4937.

[12] J.C. Stephenson, J. Chem. Phys. 59 (1973) 1523.

[13] J.C. Stephenson, J. Chem. Phys. 60 (1974) 4289.

[14] M.R. Dasilva, M.H. Vasconcelos, F. Lepoutre, M.Y. Perrin, Chem. Phys. Lett. 91 (1982) 135.

[15] M. Koshi, K. Koseki, H. Matsui, Ber. Bunsenges. Phys. Chem. 89 (1985) 309.

[16] L. Doyennette, M. Margottin-Maclou, J. Chem. Phys. 84 (1986) 6668.

[17] R.C. Millikan, D.R. White, J. Chem. Phys. 39 (1963) 3209.

[18] D.J. Miller, R.C. Millikan, J. Chem. Phys. 53 (1970) 3384.

[19] R.N. Schwartz, Z.I. Slawsky, K.F. Herzfeld, J. Chem. Phys. 20 (1952) 1591.

[20] K.F. Herzfeld and T.A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic, New York, 1959).

[21] E.E. Nikitin, S.Ya. Umanski, Faraday Discuss. Chem. Soc. 53 (1972) 1.

[22] M.P. Casassa, J.C. Stephenson, D.S. King, J. Chem. Phys. 85 (1986) 2333.

[23] M.P. Casassa, J.C. Stephenson, D.S. King, Faraday Discuss. Chem. Soc. 82 (1986) 251.

[24] M.P. Casassa, J.C. Stephenson, D.S. King, J. Chem. Phys. 89 (1988) 1966.

[25] J.R. Hetzler, M.P. Casassa, D.S. King, J. Phys. Chem. 95 (1991) 8086.

[26] R.J. Gordon, J. Chem. Phys. 74 (1981) 1676.

[27] H.K. Shin, J. Chem. Phys. 87 (1987) 993.
[28] I.R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe, I.W.M. Smith, J. Chem. Phys. 100 (1994) 4229.
[29] P.L. James, I.R. Sims, I.W.M. Smith, Chem. Phys. Lett. 272 (1997) 412.
[30] M.J. Howard, I.W.M. Smith, Prog. React. Kinet. 12 (1983) 55.
[31] I.W.M. Smith, J. Chem. Soc. Faraday Trans., in press (1997).

[32] R.P. Fernando, I.W.M. Smith, Chem. Phys. Lett. 66 (1979) 218.
[33] R.P. Fernando, I.W.M. Smith, J. Chem. Soc. Faraday Trans. 77 (1981) 459.
[34] I.W.M. Smith, M.D. Williams, J. Chem. Soc. Faraday Trans. 81 (1985) 1849.
[35] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, The Molecular Theory of Gases and Liquids (Wiley, New York, 1954).

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